

Exact Results For The Adsorption Of A Semiflexible Copolymer Chain In Three Dimensions

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Lattice model of directed self avoiding walk has been solved analytically to investigate adsorption desorption phase transition behaviour of a semiflexible sequential copolymer chain on a two dimensional impenetrable surface perpendicular to the preferred direction of the walk of the copolymer chain in three dimensions. The stiffness of the chain has been accounted by introducing an energy barrier for each bend in the walk of the copolymer chain. Exact value of adsorption desorption transition points have been determined using generating function method for the cases in which one type of monomer is having interaction with the surface viz., (i) no interaction (ii) attractive interaction and (iii) repulsive interaction. Results obtained in each of the case show that for stiffer copolymer chain adsorption transition occurs at a smaller value of monomer surface attraction than a flexible copolymer chain. These features are similar to that of a semi-flexible homopolymer chain adsorption.

1 Introduction

Biopolymers (*DNA* and *Proteins*) are known to exhibit under different physiological conditions a variety of persistent lengths ranging from being much smaller than the over all length of the polymer chain, to being comparable to the polymer chain length [1, 2]. The persistent length of biopolymers is in between the flexible and stiff polymer chains therefore biopolymers are said to be semiflexible. In addition to it such polymers are made of different type of monomers. These monomers are randomly distributed along the polymer chain length. Therefore, biopolymers are random copolymers. For example, protein molecules are composed of heterogeneous sequence of hydrophobic and hydrophilic residues and therefore proteins can be considered as a random copolymer. The conformational properties of such polymer chains have attracted considerable attention in past few years because of advancement in the experimental methods in which it has become possible to pull and stretch such single bio-molecule to measure its elastic properties [3, 4]. These study reveal a wealth of information about the conformational behaviour of biopolymers and therefore of biological importance.

Interest in copolymer chains are not only due to their application in biological physics but also due to their other variety of applications. For example, application of copolymer is in the field of biosensors, pattern recognition based application, adhesion, surface protection. In addition to it, study of adsorption of the copolymer chain on a surface is also useful in determining the relation between their composition with their adsorption characteristics.

Conformational properties of a linear homopolymer chain in dilute solution have been extensively studied [5] and its adsorption on surface has also been a well understood problem [6, 7, 8, 9, 10]. In past few years sequential copolymer adsorption in

two dimension has also received attention [11] due to location of its adsorption transition point and calculation of crossover exponent. The problem of random copolymer adsorption has been extensively studied using numerical methods; for instance, see, [12, 13, 14, 15, 16, 17] and references therein. However, analytical methods for adsorption of copolymer chain with self avoidance effect are limited to directed walk like models [11]. The study of adsorption of such copolymer chain merits somewhat differently from homopolymer case in the sense that different type of monomers of the copolymer chain need not have attractive interaction with the surface.

The essential physics associated with the behaviour of a surface interacting polymer chain in a good solvent can be derived using a model of self-avoiding walk (SAW) on a suitable lattice. If surface is attractive, it contributes an energy ϵ_s (< 0) for each step of walk lying on the surface. This leads to an increased probability defined by a Boltzmann weight $\omega = \exp(-\epsilon_s/k_B T)$ of moving a step on the surface ($\epsilon_s < 0$ or $\omega > 1$, T is temperature and k_B is the Boltzmann constant). For $\omega < \omega_c$ polymer chain is found in desorbed phase and it gets adsorbed for $\omega > \omega_c$. The polymer chain gets adsorbed on the surface at a suitable value of ϵ_s . The transition between these two regimes (adsorbed and desorbed) is marked by a critical value of adsorption energy or ω_c . One may define the crossover exponent ϕ at the adsorption transition point as, $N_s \sim N^\phi$, where N is the total number of monomers in the polymer chain and N_s the number of monomers adsorbed on the surface.

In this paper, we have extended lattice model of directed self avoiding walk introduced by Privman *et al.* [18] for homopolymer chain, to study the adsorption properties of a semiflexible copolymer chain immersed in a good solvent in three dimensions and also to examine the question whether such copolymers differ from homopolymers with respect to their critical behaviour. However, directed walk model has been used by Privman *et al.* [18] to describe rod-coil transition of a linear polymer chain and analysing the appropriate scaling properties of the polymer chain in rod-coil transitions. Mishra *et al.* [19] used definition of Privman *et al.* [18] of directed walk model to study adsorption behavior of the semiflexible polymer chain.

We have considered semiflexible sequential copolymer chain composed of two type of monomers (A & B). Such copolymer model serve as a pragmatic model for actually disordered macromolecules (for example, proteins). For the adsorption of semiflexible sequential copolymer chain on an impenetrable surface perpendicular to the preferred direction of the chain we have solved the directed walk model analytically and have found exact critical value of the surface attraction for the adsorption of the copolymer chain in three dimensions.

The outline of the paper is as follows: In Sec. 2 we describe the lattice model of directed self avoiding walk for a semiflexible sequential copolymer chain and solved the partially directed and fully directed self avoiding walk models of the copolymer chain for the adsorption of the chain on an impenetrable surface perpendicular to the preferred direction of the walks of the polymer chain. Finally, in Sec. 3 we discuss the results obtained.

2 Model and method

A model of directed self-avoiding walk [18] on a cubic lattice has been used to study adsorption-desorption phase transition behaviour of a sequential copolymer chain under good solvent condition. The directed walk models are restrictive in the sense that an angle of bending has unique value that is 90° and directedness of the walk amounts to some degree of stiffness in the copolymer chain because all directions of the space are not treated equally. However, directed self avoiding walk model can be solved analytically and therefore gives the exact value of adsorption transition point

of a semiflexible copolymer chain. We consider following two cases of directedness of copolymer chain in three dimensions: In the case (i) partially directed self avoiding walk (*PDSAW*) model, walker is allowed to walk along $\pm y$ -direction, $+x$ and $+z$ directions while in the case (ii) fully directed self avoiding walk (*FDSAW*) model, the walker is allowed to take steps along $+x$, $+y$ and $+z$ directions only.

The stiffness in the sequential copolymer chain has been introduced by associating an energy barrier for each bend in the walk of copolymer chain. The stiffness weight $k = \exp(-\beta\epsilon_b)$ where $\beta = (k_B T)^{-1}$ is inverse of the temperature and $\epsilon_b(> 0)$ is the energy associated with each bend of the walk of copolymer chain. For $k = 1$ or $\epsilon_b = 0$ the copolymer chain is said to be flexible and for $0 < k < 1$ or $0 < \epsilon_b < \infty$ the copolymer chain is said to be semiflexible. However, when $\epsilon_b \rightarrow \infty$ or $k \rightarrow 0$, the copolymer chain has a rigid rod like shape.

The partition function of a semiflexible sequential copolymer chain made of two type of monomers (A & B) can be written as,

$$Z(x_1, x_2, k) = \sum_{N=0}^{N=\infty} \sum_{\text{all walks of } N \text{ steps}} x_1^{N/2} x_2^{N/2} k^{N_b} \quad (1)$$

where, N_b is the total number of bends in a walk of N steps (monomers), x_1 and x_2 is the step fugacity of each monomer of A and B type monomers respectively. For the sake of mathematical simplicity we have taken here onwards $x_1 = x_2 = x$.

In the three dimensional directed walk model, one can consider two distinct surfaces; one parallel and the other perpendicular to the directedness of the walks of the copolymer chain. In the case of homopolymer chain adsorption on an attractive impenetrable surface, it has been found that the features associated with the adsorption were same in the case of both the surface orientations of directed polymer chain and similarity is also found in between isotropic and directed walk models of the homopolymer chain [19]. However, critical value of surface attraction for adsorption of isotropic chain is different than the directed polymer chain. Here, we report the results found using generating function method for the adsorption of directed semiflexible sequential copolymer chain on a surface perpendicular to the direction of directedness of the polymer chain in three dimensions.

In the case of three dimensional space, surface is of two dimensions i. e., a $x - y$ plane located at $z = 0$. The walker is allowed to walk along $+x$, $\pm y$ and $+z$ directions in the three dimensional space. The sequential copolymer chain is made of two type monomers, (A & B). If first monomer (step) of the copolymer chain (walk), which is grafted to the surface is of A-type then the component of partition function with initial step along $+x$ direction can be written as S_{1x} and other component with first step along any one out of $\pm y$ directions as S_{1y} . Similarly, if B-type monomer is the first monomer of the copolymer chain and it is grafted on the surface. In this situation, if first monomer (step) of the polymer chain (walk) is along $+x$ direction, the component of partition function is written as S_{2x} and S_{2y} is the component of partition function with first monomer of the copolymer chain which is B-type having first step along any one out of $\pm y$ directions. Z is component of generating function perpendicular to the plane of surface.

2.1 Adsorption of a semiflexible copolymer chain on a surface perpendicular to one out of the two preferred direction of the walk in three dimensions (*PDSAW* model).

Partition function of a surface interacting copolymer chain can be calculated using the method of analysis discussed by Mishra *et al.*, [19] and components of the parti-

tion function $Z_{PD-C}(k, \omega_1, \omega_2, x)$ of the copolymer chain interacting with the surface having first monomer of A type can be written as follows:

$$S_{1x}(k, \omega_1, \omega_2, x) = s_1 + \frac{s_1(s_2 + 2kS_{2y} + kZ)}{1 - s_1s_2} + \frac{s_1s_2(s_1 + 2kS_{1y} + kZ)}{1 - s_1s_2} \quad (s_1s_2 < 1) \quad (2)$$

where, $s_1(= \omega_1x)$ is the Boltzmann weight of interaction energy of A type monomer with the surface and similarly $s_2(= \omega_2x)$ is that of B type monomer.

$$S_{1y}(k, \omega_1, \omega_2, x) = s_1 + \frac{s_1(s_2 + 2kS_{2x} + kZ)}{1 - s_1s_2} + \frac{s_1s_2(s_1 + 2kS_{1x} + kZ)}{1 - s_1s_2} \quad (s_1s_2 < 1) \quad (3)$$

and components of the partition function with first monomer of B type is,

$$S_{2x}(k, \omega_1, \omega_2, x) = s_2 + \frac{s_2(s_1 + 2kS_{1y} + kZ)}{1 - s_1s_2} + \frac{s_1s_2(s_2 + 2kS_{2y} + kZ)}{1 - s_1s_2} \quad (s_1s_2 < 1) \quad (4)$$

$$S_{2y}(k, \omega_1, \omega_2, x) = s_1 + \frac{s_2(s_1 + 2kS_{1x} + kZ)}{1 - s_1s_2} + \frac{s_1s_2(s_2 + 2kS_{2x} + kZ)}{1 - s_1s_2} \quad (s_1s_2 < 1) \quad (5)$$

while component perpendicular to the plane of the surface is [19],

$$Z(k, x) = -\frac{x + (2k - 1)x^2}{(-1 - k + 4k^2)x^2 + (k + 2)x - 1} \quad (6)$$

On solving Eqs. (2-5) and using value of Z from Eq. (6), we get value of S_{1x} and S_{1y} ,

$$S_{1x}(k, \omega_1, \omega_2, x) = -\frac{s_1(-1 + u_1s_2 + u_2s_1s_2^2)(-1 + 2x + (-1 + 2k^2)x^2)}{(1 - 2s_1s_2(1 + 2k^2) + s_1^2s_2^2(1 - 2k^2)^2)u_3} \quad (s_1s_2 < 1) \quad (7)$$

where, u_1 , u_2 and u_3 are:

$$u_1 = -1 + s_1 + 2k^2s_1 - 2k(1 + 2s_1)$$

$$u_2 = 1 - 2k - 2k^2 + 4k^3$$

$$u_3 = (-1 - k + 4k^2)x^2 + (k + 2)x - 1$$

and

$$S_{1y}(k, \omega_1, \omega_2, x) = -\frac{(-s_1 + s_1s_2u_4 + u_5s_1s_2^2)(-1 + 2x + (-1 + 2k^2)x^2)}{(1 - 2s_1s_2(1 + 2k^2) + s_1^2s_2^2(1 - 2k^2)^2)u_3} \quad (s_1s_2 < 1) \quad (8)$$

where,

$$u_4 = -1 + s_1 + 2k^2s_1 - k(1 + 2s_1)$$

$$u_5 = 1 - k - 2k^2 + 2k^3$$

Thus, the partition function of the copolymer chain having first monomer of A type and grafted to the surface can be written as,

$$Z_{PD-C}(k, \omega_1, \omega_2, x) = S_{1x} + 2S_{1y} + Z \quad (s_1s_2 < 1) \quad (9)$$

where,

$$Z_{PD-C}(k, \omega_1, \omega_2, x) = \frac{(u_6 + u_7 + s_1^2s_2(-24k^5s_2x^2 + (-1 + x)u_8 + u_9))}{(1 - 2s_1s_2(1 + 2k^2) + s_1^2s_2^2(1 - 2k^2)^2)u_3} \quad (10)$$

here,

$$\begin{aligned}
u_6 &= x(-1 + x - 2kx) + s_1(-3 + 6x + (-3 + 6k^2)x^2) \\
u_7 &= s_2(-3 + 8x - 5x^2 + 16k^3x^2 + 2k^2x(2 + x) + k(-4 + 8x)) \\
u_8 &= -3 - 3s_2 + 3x + 4s_2x \\
u_9 &= 8k^3u_{10} + 4k^4xu_{11} - 2ku_{12} - 2k^2u_{13} \\
u_{10} &= s_2 - 2s_2x + 2x^2 + 3s_2x^2 \\
u_{11} &= -3x + s_2(-1 + 4x) \\
u_{12} &= 4(-1 + x)^2 + s_2(2 - 4x + 3x^2) \\
\text{and} \\
u_{13} &= -3 + 6x + s_2(3 - 8x + 8x^2)
\end{aligned}$$

Singularities appearing in Eq. (10) give the critical value of $x_c = \frac{k+2-\sqrt{17k}}{2(1+k-4k^2)}$ [19] and

$\omega_{c1} = \frac{4(1+k-4k^2)^2}{(1+\sqrt{2k})^2(k+2-\sqrt{17k})^2\omega_{c2}}$. On substitution of $\omega_{c1} = \omega_{c2} = \omega_c$, we are able to obtain ω_c required for adsorption of a semiflexible homopolymer chain for $3D - PDSAW$, as reported by Mishra *et al.* [19].

We consider value of ω_{c2} equal to one, greater than one (say, 1.5) and less than one (say, 0.5) depending on the fact that B-type monomer is having no interaction, attractive or repulsive interaction with the surface and obtain ω_{c1} required for adsorption of the copolymer chain on the surface. Variation of ω_{c1} is shown for different values of $\beta\epsilon_b$ for three values of ω_{c2} in Fig. (1).

(ii) *Fully directed self avoiding walk model:*

Partition function $Z_{FD-C}(k, \omega_1, \omega_2, x)$ for this case can be easily evaluated following the method used for $3D - PDSAW$ model, discussed above. We write components of the partition function $Z_{FD-C}(k, \omega_1, \omega_2, x)$ of a semiflexible sequential copolymer chain having first monomer of A type as,

$$S_{1x}(k, \omega_1, \omega_2, x) = s_1 + \frac{s_1(s_2 + kS_{2y} + kZ)}{1 - s_1s_2} + \frac{s_1s_2(s_1 + kS_{1y} + kZ)}{1 - s_1s_2} \quad (s_1s_2 < 1) \quad (11)$$

$$S_{1y}(k, \omega_1, \omega_2, x) = s_1 + \frac{s_1(s_2 + kS_{2x} + kZ)}{1 - s_1s_2} + \frac{s_1s_2(s_1 + kS_{1x} + kZ)}{1 - s_1s_2} \quad (s_1s_2 < 1) \quad (12)$$

and components of partition function with monomer grafted on the surface of B type are,

$$S_{2x}(k, \omega_1, \omega_2, x) = s_2 + \frac{s_2(s_1 + kS_{1y} + kZ)}{1 - s_1s_2} + \frac{s_1s_2(s_2 + kS_{2y} + kZ)}{1 - s_1s_2} \quad (s_1s_2 < 1) \quad (13)$$

$$S_{2y}(k, \omega_1, \omega_2, x) = s_1 + \frac{s_2(s_1 + kS_{1x} + kZ)}{1 - s_1s_2} + \frac{s_1s_2(s_2 + kS_{2x} + kZ)}{1 - s_1s_2} \quad (s_1s_2 < 1) \quad (14)$$

and component perpendicular to the surface is,

$$Z(k, x) = -\frac{x}{-1 + x(1 + 2k)} \quad (15)$$

On solving Eqs. (11-14) and substituting value of Z from Eq. (15) we get following values of S_{1x} and S_{1y} ,

$$S_{1x}(k, \omega_1, \omega_2, x) = S_{1y}(k, \omega_1, \omega_2, x) = -\frac{s_1(1 + s_2 + ks_2)(-1 + x + kx)}{(-1 + (1 + k)^2s_1s_2)(-1 + x + 2kx)} \quad (s_1s_2 < 1) \quad (16)$$

$$Z_{FD-C}(k, \omega_1, \omega_2, x) = S_{1x} + S_{1y} + Z \quad (17)$$

so that,

$$Z_{FD-C}(k, \omega_1, \omega_2, x) = \frac{x - s_1 u_{14}}{(-1 + (1+k)^2 s_1 s_2)(-1 + x + 2kx)} \quad (s_1 s_2 < 1) \quad (18)$$

where,

$$u_{14} = 2(-1 + x + kx) + (1+k)s_2(-2 + 3(1+k)x)$$

Singularities of the partition function, in this case give the critical value of $x_c = \frac{1}{2k+1}$ [19] and $\omega_{c1} = \frac{(2k+1)^2}{\omega_{c2}(k+1)^2}$. Assuming, ω_{c2} equal to one, greater than one (say, 1.5, an attractive interaction of B-type monomers with the surface) and less than one (say, 0.5, a repulsive interaction of B-type monomers with the surface), we obtained $\omega_{c1} \geq 1$ so that adsorption of copolymer chain may take place on the surface. Variation of ω_{c1} with bending energy of the copolymer chain is shown in Fig. 1 for *FDSA*W model on cubic lattice. In this case too, on substitution of $\omega_{c1} = \omega_{c2} = \omega_c$, we are able to reproduce value of ω_c required for adsorption of the semiflexible homopolymer chain, as reported by Mishra *et al.* [19] for *FDSA*W model on the cubic lattice.

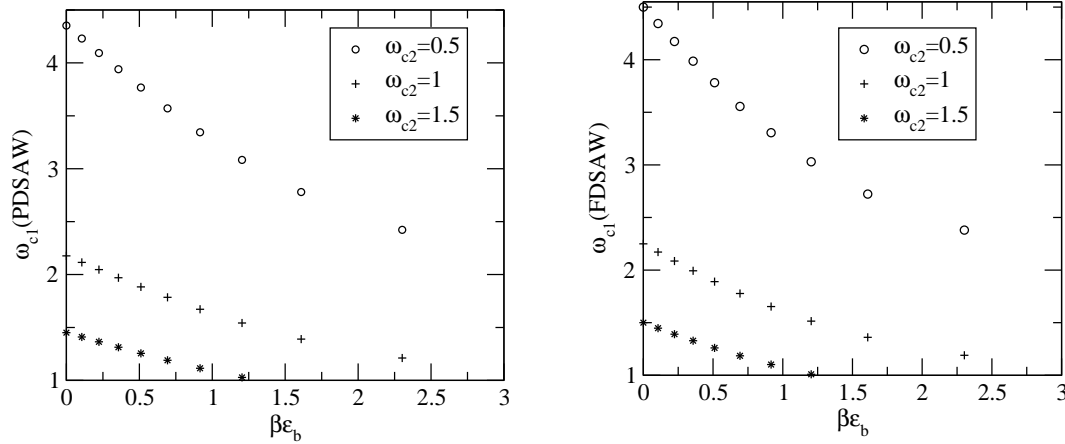


Figure 1: This figure compares the values of ω_{c1} for different values of $\beta\epsilon_b$ for adsorption of a semiflexible sequential copolymer chain on a surface perpendicular to one of the preferred directions of the copolymer chain for *PDSA*W and *FDSA*W models for three values of $\omega_{c2} = 0.5, 1 \& 1.5$.

3 Result and discussion

Directed self avoiding walk model for a semiflexible sequential copolymer chain has been solved analytically in three dimension under good solvent condition. For three dimensional space the surface considered is a two dimensional impenetrable plane and the copolymer chain is made of two type of monomers (A & B) and walk of the copolymer chain is directed perpendicular to the plane of surface. The monomers of the copolymer chain are interacting with surface. Using generating function technique, we have obtained critical value of monomer surface attraction required for adsorption of the directed copolymer chain on the surface. The dependence of the critical value of surface attraction on the stiffness of the copolymer chain has been

evaluated for the cases in which one type of monomer of the copolymer chain is having attractive interaction, repulsive interaction or no interaction with the surface. Our study showed that adsorption of a stiffer copolymer chain takes place at smaller value of monomer surface attraction when compared to that of a flexible copolymer chain. These features are similar to the semiflexible homopolymer adsorption [19].

The observed feature that stiff chain adsorption occurs at a smaller value of monomer surface attraction than the flexible chain can be understood on physical ground in following manner. The adsorption desorption phase transition behaviour of the polymer chain is result of competition between the gain in internal energy to the polymer chain due to surface attraction and loss of the entropy of the chain due to presence of the surface close to the chain. Stiffer chain has less entropy than flexible polymer chain, therefore, entropy loss is small when stiffer chain adsorbs onto the surface than the flexible chain. That is why the stiff chain adsorbs onto the surface at a smaller value of monomer surface attraction than the flexible polymer chain.

In this calculation we have considered step fugacity of both type of monomers same, i. e. $x_1 = x_2 = x$. However, this calculation can also be done using method of analysis discussed here for the case $x_1 \neq x_2$. The details of mathematical parts of this work are planned to be published elsewhere.

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